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WAVEFUNCTIONS FOR THE OZONE MOLECULE

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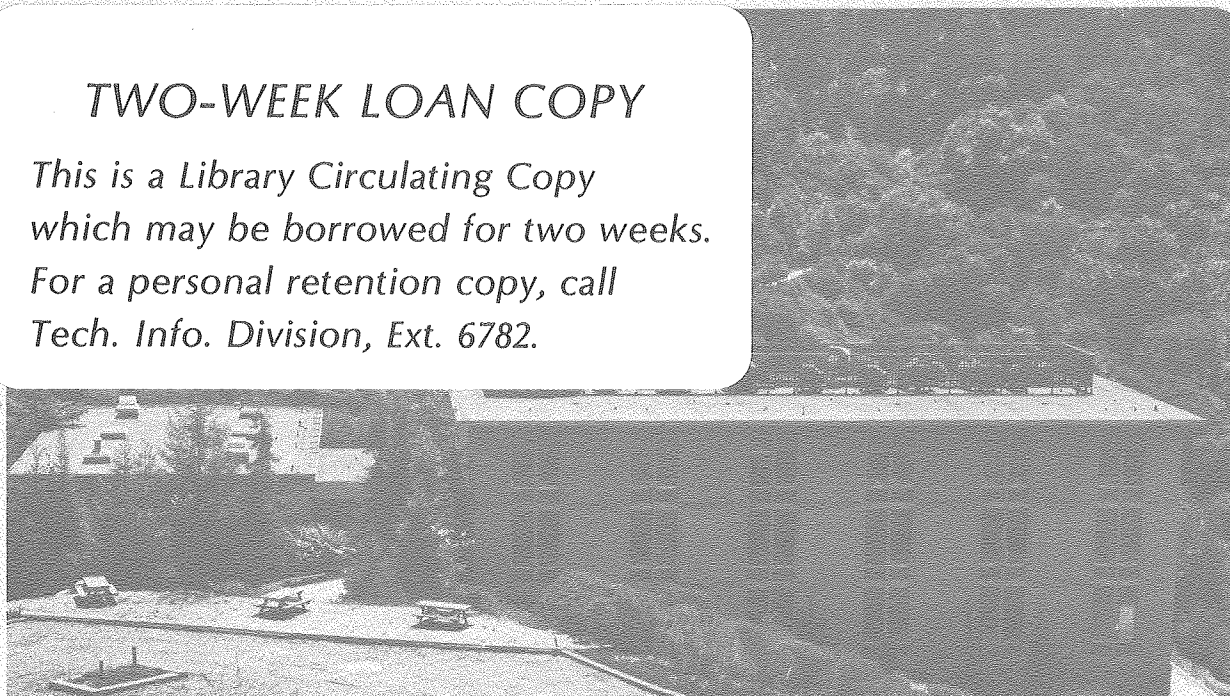
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Large Multiconfiguration Self-Consistent-Field
Wavefunctions for the Ozone Molecule

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Abstract

The electronic structure of the ozone molecule is of particular interest in light of Goddard's characterization of the ground state as a biradical. Rigorously optimized multiconfiguration self-consistent-field (MCSCF) wavefunctions of varying size have been determined here for ozone via newly developed techniques utilizing the unitary group approach. The largest of these ab initio MCSCF wavefunctions includes 13,413 configurations, i.e., all singly- and doubly-excited configurations relative to the two reference configurations required for the biradical description of ozone. The convergence of the MCSCF procedures is discussed, as well as the structure of the MCSCF wavefunctions, and the effectiveness of different orbital transformations. There is a significant energy difference (0.034 hartrees) between the MCSCF wavefunctions involving one and two reference configurations. This gives emphasis to the fact that orbital optimization alone cannot compensate for the exclusion from the wavefunction of importance classes of configurations. A simple test for the determination of the fraction biradical character of systems such as ozone suggests 23% biradical character for O_3 at its equilibrium geometry.

I. Introduction

The first multiconfiguration self-consistent-field (MCSCF) wavefunction was reported for the oxygen atom by Hartree, Hartree, and Swirles¹ in 1939. Twenty-seven years later Das and Wahl² reported the first molecular MCSCF wavefunctions, describing the H_2 , Li_2 and F_2 diatomic molecules. In the ensuing 14 years the challenge of the MCSCF problem has continued to attract the attention of outstanding theoretical chemists. Much progress has been made during this period,³⁻¹⁵ and it is

fair to say that general (i.e., involving arbitrary types of configurations) MCSCF wavefunctions involving 20 configurations may now be obtained almost routinely.

Two developments during the past year have significantly increased the range of applicability of the MCSCF method. The first is the emergence of methods which display rigorous quadratic convergence.¹⁵⁻¹⁷ In conjunction with "super CI" techniques,^{10,12-14} these second order schemes appear capable of solving even the most intractible convergence problem, long the achilles heel of the MCSCF method. The most general of the new second order methods appears capable of determining 300 configuration MCSCF wavefunctions and has already yielded an 81 configuration wavefunction for diatomic BeO.¹⁶ The second important recent development in MCSCF theory is the formulation of methods which, while restricted to first-order convergence, allow the rigorous determination of MCSCF wavefunctions more than two orders of magnitude larger than heretofore considered possible. The first of these new large MCSCF methods¹⁸ is based on the loop-driven graphical unitary

group (LDGUGA) and has been used to determine 10,115 configuration MCSCF wavefunctions for triplet cyclopropyne¹⁹ and 17,678 configuration MCSCF wavefunctions for water.²⁰ Concurrently Roos and Siegbahn have developed their complete active space (CAS) MCSCF method, which exploits the special characteristics of full CI within a limited orbital space.²¹ The largest case reported by Roos and Siegbahn to date is a 726 configuration MCSCF for the N₂ molecule, but the method should be readily applicable to much larger cases.

In most of the cases studied thus far with the LDGUGA MCSCF method, the large numbers of configurations used tend to lessen the importance of the MCSCF optimization procedure.^{19,20} Typical is an H₂O MCSCF including all configurations differing by one or two orbitals from the Hartree-Fock reference configuration, i.e., all single and double excitations. There the energy difference between the MCSCF energy and the comparable CI energy based on ordinary one-configuration SCF orbitals is only 0.000254 hartrees.²⁰ This means that in cases of this type it is hardly worth the effort required to go from the straight CI procedure to the rigorously optimum MCSCF method. It should be noted, however, that one exception to this general observation has already been found. For H₂O, when all single, double, and triple excitations are included, the MCSCF procedure results in an energy lowering of 0.004636 hartrees and a wavefunction that appears qualitatively different from the CI based on one-configuration SCF orbitals.

The purpose of the present study was to examine a system for which chemical intuition suggests a somewhat more important (than typical)

role for the MCSCF optimization procedure. One of the more obvious choices was the ozone molecule, whose electronic structure has long been of special interest.²² Several years ago Goddard and his coworkers made the important discovery that ozone has a significant amount of biradical character.^{23,24} More specifically, they stated that the ground state of O_3 can be described as a biradical with singly-occupied π orbitals on the terminal oxygen atoms singlet coupled to each other. From a slightly different vantage point this means that the Hartree-Fock wavefunction, designated

$$\Phi_1 = \dots\dots 5a_1^2 3b_2^2 1b_1^2 6a_1^2 4b_2^2 1a_2^2 \quad (1)$$

is a relatively poor approximation to the exact wavefunction. The biradical character of the ozone ground state may be seen in the large weight of the second configuration

$$\Phi_2 = \dots\dots 5a_1^2 3b_2^2 1b_1^2 6a_1^2 4b_2^2 2b_1^2 \quad (2)$$

For example, the present two-configuration (TC) SCF wavefunction for O_3 provides coefficients $C_1 = 0.876$, $C_2 = -0.481$ for the relative weights of these two coefficients. In this picture the Hartree-Fock configuration (1) represents only 77% of this TCSCF wavefunction, compared to 95% for more typical closed-shell ground states. Therefore the goal of our research was to examine how this biradical character of ozone manifests itself in the context of large MCSCF wavefunctions.

II. Theoretical Approach

A reasonably standard treatment²⁵⁻²⁷ of electron correlation in the ozone ground state would be the following:

- (a) Obtain a two-configuration SCF wavefunction.
- (b) Using this TCSCF set of molecular orbitals, carry out configuration interaction (CI) including all singly- and doubly-excited configurations relative to both reference configurations determined in (1).

Such a procedure will surely give a reasonable picture of the electronic structure of O_3 .

However, it occurred to us that in the context of fully optimized, large MCSCF wavefunctions, a simpler wavefunction might be nearly as complete. In particular, we wanted to investigate the effectiveness of an MCSCF wavefunction including all single and double excitations relative to (1) only. Since configuration (2) is a double excitation ($1a_2^2 \rightarrow 2b_1^2$) with respect to (1), it will automatically be included in such a wavefunction. Furthermore, the MCSCF procedure guarantees that configuration (2) will come in with its weight (CI coefficient) and orbitals determined to as to yield the lowest possible energy for the complete wavefunction.

Of course, what is primarily missing from the wavefunction described in the previous paragraph are the single and double excitations relative to (2). Our thinking was that these might not be so important as long as the orbitals and CI coefficient of (2) were given complete variational flexibility in the large, one reference MCSCF. In a more general perspective, then, one is asking the question, "can the variational

freedom of the MCSCF procedure make up for what would otherwise (i.e., using straight configuration interaction techniques) be a deficiency in the form of the wavefunction?".

The geometry used here for O_3 was $r(O-O) = 1.271 \overset{\circ}{\text{\AA}}$, $\theta(000) = 116.8^\circ$. A more precise geometry is specified by the cartesian coordinates of the two terminal O atoms, namely $(0, \pm 2.0457412, 1.2585484)$ in atomic units. This structure is quite close to the experimental geometry²⁸ $r_0(O-O) = 1.278 \overset{\circ}{\text{\AA}}$, $\theta_0(000) = 116.8^\circ$.

Since our purposes were primarily methodological and qualitative, a large basis set was not deemed mandatory in this work. Therefore the standard contracted gaussian double zeta basis of Huzinaga and Dunning was chosen.²⁹ Such a basis includes two 1s, two 2s, and two each $2p_x$, $2p_y$, and $2p_z$ functions on each oxygen atom and may be designated³⁰ $O(9s5p/4s2p)$.

III. Wavefunctions and Energies for Ozone

A. One and Two-Configuration SCF

The one-configuration SCF energy for O_3 at the chosen geometry and with the standard double zeta basis set was -224.2077 hartrees. The comparable two-configuration SCF energy is -224.3104 hartrees, or a remarkable 0.1027 hartrees lower than the one configuration result. This energy lowering and the TCSCF coefficients ($C_1 = 0.876$, $C_2 = -0.481$) are of course consequences of the biradical character of O_3 established by Hay, Dunning, and Goddard²⁴ nearly ten years ago.

B. CI Based on One Reference Configuration

All the CI and MCSCF wavefunctions reported here were obtained via the loop-driven graphical unitary group approach.^{31,32} When all single and double excitations are taken relative to (1), a total of 6,825 1A_1 configurations is generated. Using the ordinary one-configuration (OC) SCF orbitals, the CI energy obtained is -224.6139 hartrees. The coefficients of the the most important configurations are $C_1 = 0.933$ and $C_2 = -0.149$. The smallness of the latter coefficient (e.g., compared to the TCSCF result $C_2 = -0.481$) gives little indication of the significant fraction of O_3 biradical character.

C. MCSCF Based on One Reference Configuration

The first large MCSCF wavefunction for ozone included the same 6,825 configurations discussed in the previous paragraph. The MCSCF energy was -224.6155 hartrees, or 0.0016 hartrees below the comparable straight CI result. This energy lowering was about six times greater than for the analogous H_2O calculations, but much less than that anticipated for O_3 in Section II above. Furthermore, the weight of configuration (2) increases only marginally from $C_2 = -0.149$ to $C_2 = -0.162$ in going from the straight CI to the 6825 configuration MCSCF wavefunction. Thus the biradical nature of ground state ozone is not particularly apparent even in this large MCSCF wavefunction.

The fact that a second large configuration does not surface in the one reference MCSCF deserves special attention. Since all configurations of the form $la_2^2 \rightarrow nb_1^2$, and $la_2^2 \rightarrow nb_1 mb_1$ are included in the MCSCF wavefunction, there may be no particular significance to the $2b_1$ orbital (other than its resemblance to the $2b_1$ OCSCF orbital, from which the MCSCF iterations began). In such cases the sum of the weights of all such configurations should be a more reasonable quantity to examine. Alternately, the natural orbitals derived from such an MCSCF wavefunction would provide a unique $2b_1$ orbital.

D. CI Based on Two Reference Configurations

All single and double excitations relative to both (1) and (2) comprises a total of 13,413 1A_1 configurations. Even using the OCSCF orbitals, the biradical character of O_3 becomes apparent when this CI is carried out. The leading coefficients in this 13,413 configuration wavefunction are $C_1 = 0.894$ and $C_2 = -0.296$. Therefore it is apparent that the single and double excitations relative to the second O_3 configuration (2) are required to obtain a correct qualitative picture of the electronic structure. The energy of this larger CI wavefunction was -224.6402 hartrees, which is 0.0263 hartrees below the one reference CI energy and 0.0247 hartrees below the one reference (6825 configurations) MCSCF energy. It is seen that the MCSCF procedure recovers only a small fraction (6%) of the difference between the one and two reference CI energies.

It was also considered instructive to carry out the 13,413 configuration CI in terms of the TCSCF orbitals. As expected these TCSCF orbitals are more suitable for the two-reference CI than were the OCSCF orbitals. More specifically, the total energy obtained was -224.6476, or 0.0072 hartrees below the comparable CI energy based on OCSCF orbitals. Also as expected, the second configuration takes on a greater weight in the CI ($C_2 = -0.3553$) when the TCSCF orbitals are employed.

E. MCSCF Based on Two Reference Configurations

The MCSCF procedure to determine the 13,413 configuration SCF wavefunction was initiated with the MCSCF orbitals from the converged

6,825 configuration wavefunction. Since the electronic structure of the larger MCSCF turns out to be quite different from that of the MC6825 wavefunction, this may not have been the best starting point. Nevertheless, the MC13413 energy converged to within 10^{-4} hartrees in four iterations, to 10^{-5} hartrees in six iterations, to 10^{-6} hartrees in nine iterations, and to 10^{-7} hartrees in twelve iterations. Since this pattern of convergence is rather similar to that observed for MC6825 starting out the OCSCF orbitals, it may be reasonably independent of the set of starting orbitals, assuming some sort of a sensible choice is made.

For MC13413, one finds $C_1 = 0.887$, $C_2 = -0.337$. Since this is the best ozone wavefunction determined here, it provides a framework for our final estimate of the biradical character of the O_3 ground state. For a "perfect" or 100% biradical, one would have $C_1 = -C_2 = 1/\sqrt{2} = 0.707$. It is not then unreasonable to define the fraction B of biradical character as³³

$$B = \frac{C_2^2}{(1/\sqrt{2})^2} = 2 C_2^2 \quad (3)$$

With this definition, the 13,413 configuration MCSCF wavefunction has $B = 0.227$, corresponding to 22.7% biradical character. By the same standard the one reference (6825 configurations) MCSCF severely underestimates the biradical fraction, suggesting $B = 0.053$, or only 5.3% biradical character. However, the two-configuration SCF wavefunction overestimates the biradical character of O_3 by an even greater amount, suggesting $B = 0.464$. Any biradical wavefunction may be subjected to the same test and it is apparent that B will depend on both basis set

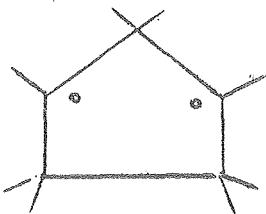
and the type of CI or MCSCF procedure chosen. For example, Hay and Dunning's 1557 configuration CI wavefunction³⁴ for ozone (obtained with a double zeta plus polarization basis set) has $C_2 = -0.319$ and hence $B = 0.204$, or 20.4% biradical character. The reasonable agreement with our prediction of 23% suggests qualitative consistency between B values obtained from properly designed wavefunctions for ozone.

The total energies of MC13413 and all the other wavefunctions reported here are given in the Table. The energy of the former is -224.6493 hartrees, or 0.0091 hartrees lower than CI13413 based on OCSCF molecular orbitals. However the energy of this large MCSCF wavefunction is only 0.0017 hartrees below that of CI13413 based on the TCSCF orbitals. This comparison emphasizes the superiority of the TCSCF orbitals in such a large CI^{25,27} and shows that the complete and rigorous optimization inherent in the MCSCF procedure is probably not required for most applications of this type.

However it is interesting to note the interrelationship between entries 3 and 4 of the Table and the last two entries. The respective energy lowerings due to the MCSCF procedure are 0.0016 hartrees and 0.0017 hartrees, i.e., comparable. This is surprising since the latter two-reference CI space is much more complete than the former one-reference space. In general, one expects the MCSCF procedure to yield greater energy lowerings (relative to straight CI) when a less complete set of configurations is employed. It is apparent that more experience with large MCSCF procedures will be necessary before one can anticipate the outcome with confidence.

IV. Concluding Remarks

Large MCSCF wavefunctions (up to 13,413 configurations) have been reported for the ozone molecule. These suggest a biradical character of about 23%, much greater than that for methylene,^{25,27} but much less than that for the nearly "perfect" cyclopentadiyl biradical^{35,36}



(4)

For the ozone molecule at its ground state equilibrium geometry, these large MCSCF wavefunctions represent relatively little improvement (about 1 kcal) in total energy relative to the comparable straight CI based on orbitals from the much simpler two-configuration SCF wavefunction. However, there are many systems such as (4) or any number of molecules at geometries far from equilibrium, where the Hartree-Fock approximation is much poorer than for ozone. For some of these it seems likely that large MCSCF procedures will be valuable. In addition such large MCSCF wavefunctions, for which the energy is stationary with respect to both the molecular orbitals and CI coefficients, should lend themselves fairly readily to the analytic evaluation of force constants, i.e., second derivatives of the total energy with respect to displacements of the nuclear coordinates.

V. Acknowledgments

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36. Specific values for biradical character are not cited here, since CH_2 and C_5H_8 have not been treated at a level of theory comparable to that employed here for ozone. However the relationship $B(\text{cyclopentadiyl}) > B(\text{ozone}) > B(\text{methylene})$, based on TCSCF wavefunctions, should hold up as the level of theoretical sophistication is raised.

Table. Summary of large MCSCF results for the 1A_1 ground state of ozone near its equilibrium geometry.

<u>Number of Configurations</u>	<u>Description of Configurations</u>	<u>Type of Wavefunction</u>	<u>Energy (hartrees)</u>	Coefficients of Two Most Important Configurations	
				<u>C₁</u>	<u>C₂</u>
1	(1) in Text	SCF	-224.207 656	1.0000	--
2	(1) and (2) in Text	TCSCF	-224.310 437	0.8765	-0.4815
6,825	All S + D Excitations Relative to (1)	CI ^a	-224.613 929	0.9331	-0.1493
6,825	" "	MCSCF	-224.615 493	0.9343	-0.1620
13,413	All S + D Excitations Relative to (1) <u>and</u> (2)	CI ^a	-224.640 183	0.8935	-0.2957
13,413	" "	CI ^b	-224.647 645	0.8762	-0.3553
13,413	" "	MCSCF	-224.649 326	0.8870	-0.3371

^aCI used one-configuration SCF orbitals.

^bCI used two-configuration SCF orbitals.